SCIENCE FOR GLASS PRODUCTION

GLASS FORMATION, CRYSTALLIZATION, AND SPECTRAL-LUMINESCENCE PROPERTIES OF GLASSES OF THE Er_2O_3 – Yb_2O_3 – B_2O_3 – GeO_2 SYSTEM

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Borogermanate glasses with a 25% molar content of lanthanoid oxides were synthesized and investigated. It was found that their glass transition temperature t_g is about 770°C, approximately 200°C higher than the t_g of laser phosphate glass. Relatively weak clustering of erbium, whose optical centers are characterized by high homogeneity and a large (86 – 90 nm) effective half-width of the $^4I_{13/2} \to {}^4I_{15/2}$ luminescence band of Er^{3+}, is realized.

Germanate glass, which has elevated physicochemical and performance parameters, is characterized by a lower frequency position of the phonon spectrum in comparison to silicate glass, which weakens intracentric dissipation of the excitation energy of different activators and gives this glass certain advantages when they are used as active laser elements. However, due to the high cost of GeO_2, which is many times higher than the cost of SiO_2, it has not been used in practice for a long time. Interest in germinate glass has recently increased sharply due to the use of germanium for doping quartz wave guides and attempts to introduce optical communications lines with a wavelength of $\lambda \sim 2$ μm, near where GeO_2 glass has an intrinsic optical loss minimum [1]. Due to the high Raman scattering section of germinate glass (one order of magnitude higher than for quartz glass), it is also promising for creating fiber lasers that operate on the induced Raman scattering effect [1].

We investigated glass formation, crystallization, and the spectral-luminescence properties of glass of the Er_2O_3 – Yb_2O_3 – B_2O_3 – GeO_2 (EYBG) system which allows adding up to 25% (molar content) of rare-earth oxides. Coactivation of this glass with Yb^{3+} ions makes it necessary to sensitize luminescence of Er^{3+} [2], while B_2O_3 is used to increase the solubility of the rare-earth oxides [3] and accelerate the $^4I_{11/2} \to {}^4I_{13/2}$ transition [4], the "narrow neck" in the sensitized luminescence channel of glass containing erbium and ytterbium. The basic "generation" band of lasers for erbium-containing glass is due to a $^4I_{13/2} \to {}^4I_{15/2}$ transition and is located in the spectral region at $\lambda \sim 1.54$ μm. Such radiation is relatively safe for the eyes and is in the region of minimum optical losses of quartz fiber waveguides, which is also responsible for the wide use of lasers and amplifiers in erbium glass in range finders and fiber-optic communications lines.

Very pure Er_2O_3, Yb_2O_3, H_3BO_3, and GeO_2 were used as the initial components for melting the glass. The glass was melted in corundum crucibles in oxidizing conditions at 1490°C for 20 min. The glass melt was poured out of the crucible onto a metal plate and pressed with another plate to a thickness of 1.5 – 2.0 mm. Each portion of batch was calculated for 10 g of glass. According to the estimations in [5], for glass of similar compositions in the lanthanum – borogermanate (LBG) system melted in corundum crucibles at 1300 – 1350°C, the mass content of aluminum was 5 – 7%. Since the melting temperature in the present study was higher, we can predict that the mass content of aluminum

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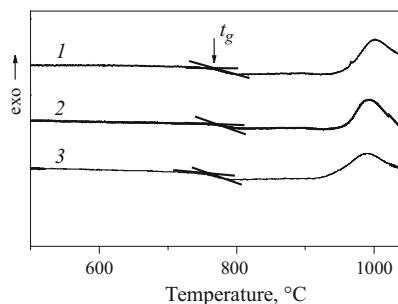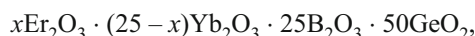[3] Scientific-Practical Center, National Academy of Sciences of Belarus on Materials Science, Minsk, Belarus.

Fig. 1. DTA curves of glass powders with a different $Er_2O_3 : Yb_2O_3$ ratio: *1*, *2*, and *3*) samples No. 1, 4, and 7.

Fig. 2. X-ray patterns of glass heat treated at 990°C for 30 min and diffraction line patterns from the electronic catalog of diffractograms: *1* and *2*) glass of composition Nos. 6 and 1, respectively; *3*) $ErBO_3$ (JCPDS 113-0486); *4*) $YbBO_3$ (JCPDS 74-1937); *5*) $Er_2Ge_2O_7$ (JCPDS 72-0745); *6*) $Yb_2Ge_2O_7$ (JCPDS 45-0531).

would be greater than 7%. The calculated compositions of the glass was:

$$x Er_2O_3 \cdot (25 - x) Yb_2O_3 \cdot 25 B_2O_3 \cdot 50 GeO_2,$$

where $x = 1, 2, 3, 4, 5, 6$, and 7% (molar content; the value of x corresponds to the numbering of the samples).

Differential thermal analysis (DTA) of powdered samples was performed with a Q-1500 derivatograph at a heating rate of 10 K/min. The x-ray patterns of the powdered samples were recorded with a DRON-3M diffractometer (CuK$_\alpha$ radiation, Ni filter).

A Cary-500 spectrophotometer and a FT-IR NEXUS spectrometer were used to record the light-attenuation spectra. The luminescence spectra were recorded on a SDL-2 spectrofluorimeter, corrected in consideration of the spectral sensitivity of the recording system, and presented in the co-ordinates: number of quanta per individual wavelength interval $dN(\lambda)/d\lambda$. Frontal excitation of the samples was used to reduce overabsorption of luminescence, and the sample thickness was decreased to 0.1 mm if necessary. The invariability of the geometric position of the samples in the recording channel allowed correctly comparing the relative intensities of their luminescence.

The DTA curves of EYBG glass with the minimum, intermediate, and maximum Er_2O_3 content are shown in Fig. 1. The glass transition temperatures t_g, determined by the tangential values method, are not a function of the $Er_2O_3 : Yb_2O_3$ ratio and are approximately 770°C. All three curves are characterized by an exothermic peak with a maximum at 990°C. Heat treatment of the glass at this temperature for 30 min caused the formation of the same set of phases, and with an increase in the erbium content but with the same $Er_2O_3 + Yb_2O_3$ molar content of 25%, the crystallizability of the glass increased (Fig. 2). The products of crystallization of these glasses were erbium and ytterbium borates and germanates. The similarity of the line diffraction patterns of erbium and ytterbium borates makes them difficult to distinguish in the x-ray pattern of the crystallized glass. The same situation is also characteristic in identification of the germinates of these rare-earth elements.
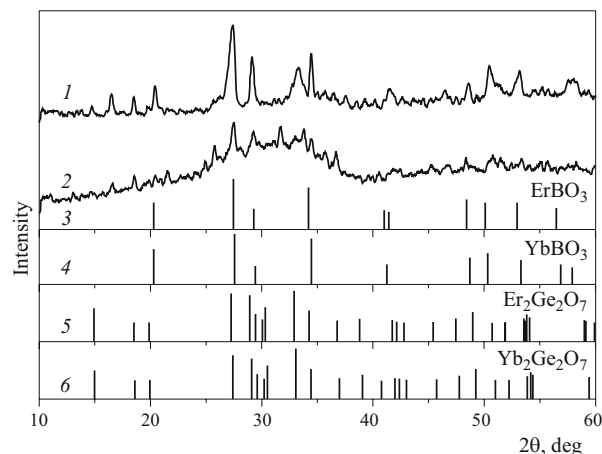
The crystallizability of glass of the EYBG system differs significantly from LBG glass of the $25 La_2O_3 - 25 B_2O_3 - 50 GeO_2$ system (molar ratio, %). A pronounced dependence of the tendency to crystallize and the conditions of synthesis was established for the latter glass [5]. In contrast to the glass from the EYBG system, the exothermic effects caused by crystallization were absent on the DTA curve of this glass melted in a corundum crucible. However, the DTA curve of the glass from the LBG system melted in a platinum crucible was characterized by a large exothermic peak at about 900°C [6]. This difference in the crystallization of glass of the LBG and EYBG systems is perhaps due to the difference in the melting temperature and consequently the intensity of corrosion of the corundum crucible, which causes a different Al_2O_3 content in these glasses. In the case of EYBG system glasses, the concentration of alumina was probably outside of the range that inhibits crystallization processes, and optimizing it allows minimizing the exothermic effect on the DTA curve and the crystallizability of the EYBG system glass by analogy with LBG system glass.

The light attenuation spectrum of sample No. 5 is shown in Fig. 3. The spectra of all other EYBG system glasses studied were similar. It is not difficult to see that the region of optical transparency of the matrix, measured for a natural absorption index of 50 cm^{-1}, overlaps the entire range from 2780 to 5680 nm. The narrow bands at $\lambda \sim 1530$ nm and shorter bands at 830 nm located in this range are due to $f-f$ transitions of Er^{3+} ions. The relatively wide band at $\lambda \sim 940$ nm with an intense narrow component at $\lambda \sim 974$ nm belongs to $^2F_{7/2} \rightarrow {}^2F_{5/2}$ transitions of Yb^{3+} ions, and the weak band at $\lambda \sim 2900$ nm (designated by the arrow in the inset) belongs to hydroxyl ions [6]. The double-hump band with maxima at $\lambda \sim 3800$ and 4400 nm can be assigned to bond vibrations in boron-containing structural groups, in
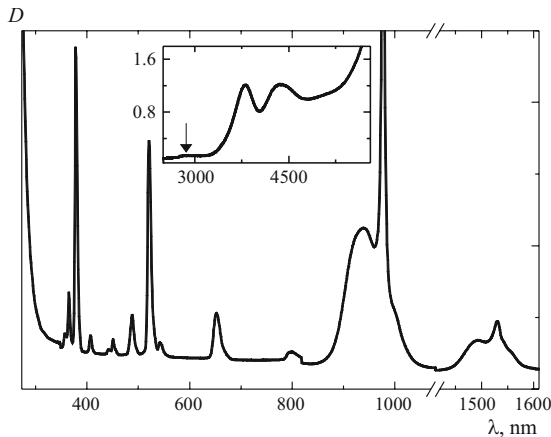
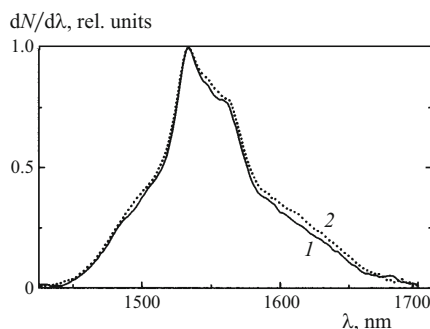**Fig. 3.** Light attenuation spectrum D of sample No. 5 0.8 mm thick.

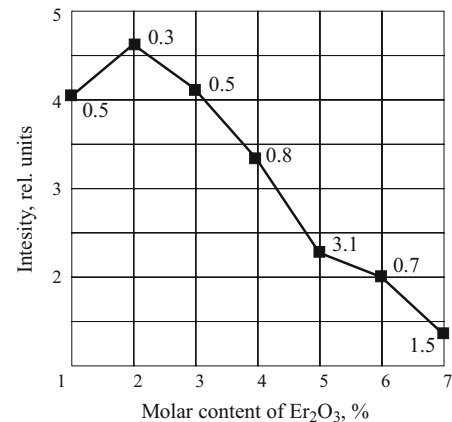**Fig. 4.** Luminescence spectra of sample No. 1 at the excitation wavelength (*1*) and at 380 nm (*2*).

Fig. 5. Intensity of luminescence of Er^{3+} ions in the $^4I_{13/2} \to {}^4I_{15/2}$ transition as a function of their concentration in glass of the EYBG system ($\lambda_{exc} = 974$ nm). The figures at the experimental points indicate the value of the natural absorption index (cm^{-1}) of hydroxyl ions at $\lambda = 2900$ nm.

consideration of the absence of such a band in germinate glass with no B_2O_3.

We should emphasize that for all of the glasses investigated, the shape of the individual spectral bands of both coactivators was preserved, while the change in the integral intensity of each band in terms of one ion did not exceed $\pm 10\%$. This suggests an important conclusion concerning the significant changes in the structure of the optical centers of Er^{3+} and Yb^{3+} as a function of the concentration of coactivators.

The luminescence spectra of sample No. 1 in the $^4I_{13/2} \to {}^4I_{15/2}$ transition of Er^{3+} ions at an excitation wavelength of $\lambda_{exc} = 974$ and 380 nm are shown in Fig. 4. These spectra almost coincide, and the effective half-width of the given band, measured as the ratio of the integral intensity to the peak intensity, is 86 and 90 nm for curves *1* and *2*. These values are much higher than the value of the same parameter for erbium-doped glass of the $TeO_2 - Na_2O - ZnO$ $(62 - 75$ nm [7]) and $TiO_2 - Al_2O_3 - TeO_2$ (less than 75 nm) systems [8] and obtained from the gas phase of glass based on SiO_2 with Al and Ge additives (about 60 nm) [9]. In scanning of λ_{exc} based on the absorption bands of both coactivators, the position of this luminescence band is preserved,

while the change in the relative intensity of its contour at the same λ does not go beyond the limits of $\pm 10\%$ for all samples. This suggests the high homogeneity of the Er^{3+} optical centers formed in this glass.

The integral intensity of the sensitized luminescence of Er^{3+} ions in the $^4I_{13/2} \to {}^4I_{15/2}$ transition as a function of their concentration in excitation in the $^2F_{7/2} \to {}^2F_{5/2}$ absorption band of Yb^{3+} ions ($\lambda_{exc} = 974$ nm) is shown in Fig. 5. The almost total absorption of the exciting radiation in the surface layer and insignificant efficacy of reverse energy transfer to the sensitizer [4] suggest that the dependence is primarily determined by "upconversion" processes from the $^4I_{13/2}$ state and its deactivation by extrinsic hydroxyl ions. In other words, the concentration of both hydroxyl and Er^{3+} ions affects the luminescence intensity.

The lower the hydroxyl group content, the higher the luminescence intensity is. The latter is maximum for a defined number of Er^{3+} ions, and with an excess of these ions, it drops due to concentration extinction. In all probability, the relatively weak erbium clustering allows incorporating up to 3% (molar content) of Er_2O_3 in the glass (see Fig. 5) without marked extinction of luminescence in the $^4I_{13/2} \to {}^4I_{15/2}$ transition. As the shape of the curve in Fig. 5 indicates, the effect of hydroxyl ions is less important and "upconversion" makes the basic contribution to the decrease in the luminescence intensity. For example, for almost the same hydroxyl concentration (0.7 and 0.8 cm^{-1}), the luminescence intensity differs strongly due to the different Er^{3+} content.

The synthesized borogermanate glass with a high total molar content of erbium and ytterbium oxides (25%) thus have a high glass transition temperature ($t_g \sim 770$°C), approximately 200°C higher than the t_g of laser phosphate glass. The relatively weak erbium clustering is a positive quality of this glass: marked extinction of luminescence in the $^4I_{13/2} \to {}^4I_{15/2}$ transition is not observed for a molar con-

tent of Er$_2$O$_3$ under 3%. The optical centers of the Er^{3+} ions in this glass are characterized by high homogeneity and a high effective luminescence band half-width (86 – 90 nm), which makes them promising as an active medium in fiber optic communications lines.

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